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## RESEARCH LETTER

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## Key Points:

- First detection of boron on Mars' surface
- Presence of boron in Gale crater suggests evaporite deposits may be present stratigraphically above the detected boron
- Borates can stabilize ribose in aqueous solutions and thus may be important for prebiotic chemistry

## Supporting Information:

- Supporting Information S1
- Data Set S1

## Correspondence to:

P. J. Gasda,  
gasda@lanl.gov

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## In situ detection of boron by ChemCam on Mars

Patrick J. Gasda<sup>1</sup>, Ethan B. Haldeman<sup>2</sup>, Roger C. Wiens<sup>1</sup>, William Rapin<sup>3</sup>, Thomas F. Bristow<sup>4</sup>, John C. Bridges<sup>5</sup>, Susanne P. Schwenzer<sup>6</sup>, Benton Clark<sup>7</sup>, Kenneth Herkenhoff<sup>8</sup>, Jens Frydenvang<sup>9</sup>, Nina L. Lanza<sup>1</sup>, Sylvestre Maurice<sup>10</sup>, Samuel Clegg<sup>1</sup>, Dorothea M. Delapp<sup>1</sup>, Veronica L. Sanford<sup>2</sup>, Madeleine R. Bodine<sup>1</sup>, and Rhonda McInroy<sup>1</sup>
<sup>1</sup>Los Alamos National Laboratory, Los Alamos, New Mexico, USA, <sup>2</sup>Chemistry Department, Ursinus College, Collegeville, Pennsylvania, USA, <sup>3</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA, <sup>4</sup>NASA Ames, Mountain View, California, USA, <sup>5</sup>Department of Physics and Astronomy, University of Leicester, Leicester, UK, <sup>6</sup>Department of Earth Science, Open University, Milton Keynes, UK, <sup>7</sup>Space Science Institute, Boulder, Colorado, USA, <sup>8</sup>USGS, Flagstaff, Arizona, USA, <sup>9</sup>Natural History Museum of Denmark, University of Copenhagen, Copenhagen, Denmark, <sup>10</sup>CNES/IRAP, Paris, France

**Abstract** We report the first in situ detection of boron on Mars. Boron has been detected in Gale crater at levels <0.05 wt % B by the NASA *Curiosity* rover ChemCam instrument in calcium-sulfate-filled fractures, which formed in a late-stage groundwater circulating mainly in phyllosilicate-rich bedrock interpreted as lacustrine in origin. We consider two main groundwater-driven hypotheses to explain the presence of boron in the veins: leaching of borates out of bedrock or the redistribution of borate by dissolution of borate-bearing evaporite deposits. Our results suggest that an evaporation mechanism is most likely, implying that Gale groundwaters were mildly alkaline. On Earth, boron may be a necessary component for the origin of life; on Mars, its presence suggests that subsurface groundwater conditions could have supported prebiotic chemical reactions if organics were also present and provides additional support for the past habitability of Gale crater.

## 1. Introduction

Boron is an intriguing element for geology and astrobiology. On Earth, boron is a highly soluble element found concentrated in phyllosilicate-bearing sediments and evaporite deposits, making boron useful for understanding surface and subsurface aqueous processes [Goldschmidt and Peters, 1932; Fredrickson and Reynolds, 1960; Hunt et al., 1966; Lerman, 1966; Couch and Grim, 1968; Harder, 1970; Perry, 1972] and in reconstructing fluid temperature and pH [Spivack et al., 1987; You et al., 1996; Goldberg, 1997; Williams et al., 2001]. Borate anions (BO<sub>4</sub><sup>−</sup>) may also be necessary for the origin of life [Scorei, 2012]. Borate anions have been shown to slow the decomposition of ribose in solution, an important prebiotic compound and component of ribonucleic acid (RNA), and mediate ribose formation [Kim et al., 2011] by the formose reaction [Boutlerow, 1861] by forming ribose-borate complexes [Ricardo et al., 2004; Scorei, 2012; Furukawa et al., 2013].

Boron and borates are potentially detectable on Mars by instruments deployed on the surface, including ChemCam [Wiens et al., 2012; Maurice et al., 2012] and CheMin [Blake et al., 2012] on *Curiosity*, or by orbital multispectral infrared remote sensing instruments [Cloutis et al., 2016]. Boron has also been detected in Martian meteorites (Table 1). Although Martian evaporite deposits have been detected by Mars Global Surveyor TES and Mars Odyssey THEMIS instruments [e.g., Osterloo et al., 2008; 2010; Hynek et al., 2015], multi-spectral imagers have not detected borates remotely as of this publication [Cloutis et al., 2016]. CheMin, the X-ray diffraction instrument on *Curiosity*, is capable of detecting borate minerals but has not detected them in any drilled or scooped samples. Thus, this detection of boron by ChemCam represents the first time boron has been observed in situ on Mars.

The NASA *Curiosity* rover is currently investigating the 5 km high sedimentary mound Aeolis Mons (informally, “Mt. Sharp”) within Gale crater [Malin, 2000; Edgett and Malin, 2001; Milliken et al., 2010; Fraeman et al., 2016]. Gale is a 155 km wide complex equatorial crater on the edge of the Mars dichotomy in northern Terra Cimmeria. *Curiosity* landed on Aeolis Palus basin in the northwestern quadrant of Gale and has traversed ~16 km from the landing site at “Bradbury Rise” to the “Upper Murray,” exploring sediments interpreted as fluvial deltaic and sandstone deposits [Grotzinger et al., 2015] and stratified lake deposits [Hurowitz et al., 2017].

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**Table 1.** Literature Summary of Boron Content in Bulk Silicate Mars and Martian Meteorites

		ppm B	References
Bulk Silicate Mars		0.6	<i>Stephenson et al.</i> [2013]
Meteorite(s)	Associated Phase		
MIL 090030	olivine	0.03	<i>Stephenson et al.</i> [2013]
Nakhla, Lafayette, MIL 090030	pyroxene	0.1–1	<i>Stephenson et al.</i> [2013], and <i>Spivak-Birndorf et al.</i> [2008b, 2008c]
Nakhla	whole rock	4.6	<i>Lodders</i> [1998]
Nakhla	melt inclusion	5	<i>Spivak-Birndorf et al.</i> [2008c]
Nakhla	mesostasis	4–7	<i>Spivak-Birndorf et al.</i> [2008c]
Nakhla and Lafayette	iddingsite	7–18	<i>Spivak-Birndorf et al.</i> [2008a, 2008b]
MIL 090030	alteration vein	154–166	<i>Stephenson et al.</i> [2013]
Chassigny	whole rock	6.3	<i>Lodders</i> [1998]

Here we show that boron is enriched relative to igneous Martian materials (Table 1) and found in several calcium-sulfate-filled fractures (henceforth called “veins,” described by *Schwenzer et al.* [2016], *Rapin et al.* [2016], and *Nachon et al.* [2014, 2017]) hosted by the “Yellowknife Bay” formation, the lacustrine “Murray” formation mudstone, and the unconformably overlying aeolian “Stimson” formation sandstone units (described in *Grotzinger et al.* [2014, 2015], *Fedo et al.* [2017], and *Banham et al.* [2017]).

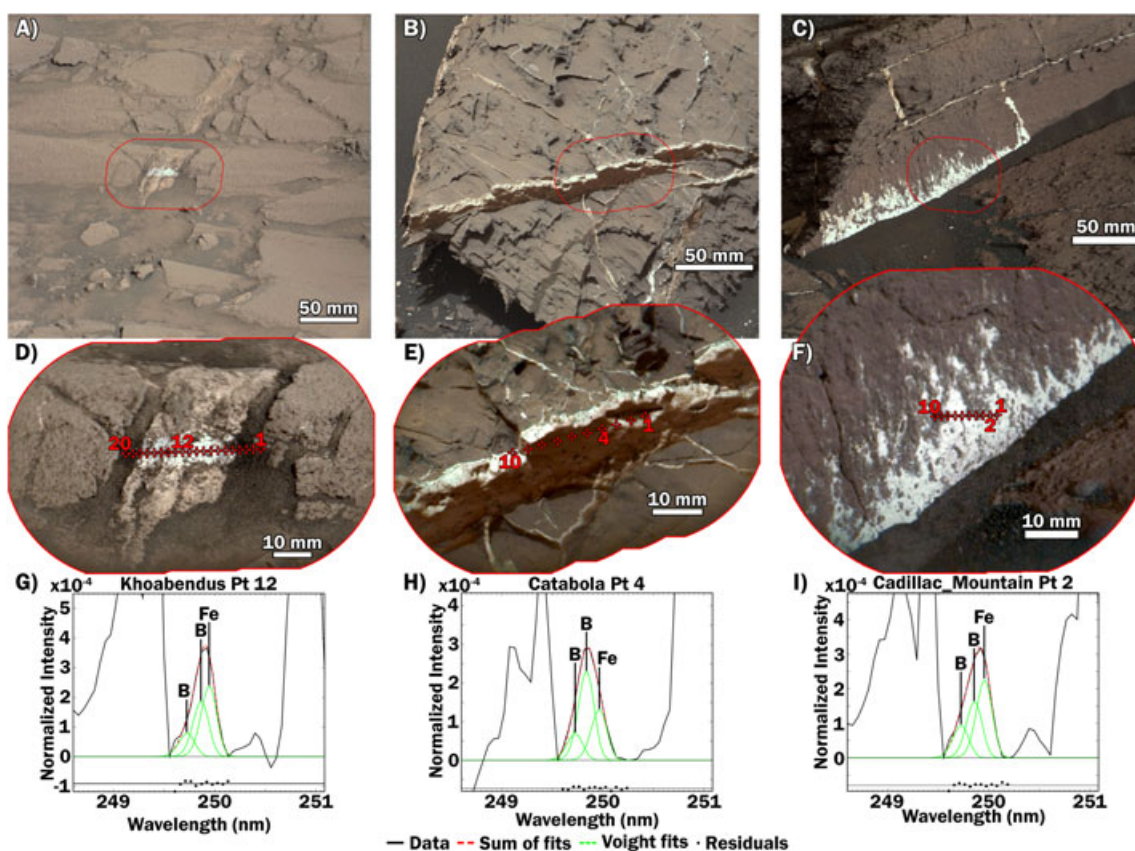
## 2. Methodology

Boron observations were made using the ChemCam instrument suite: a laser-induced breakdown spectroscopy (LIBS) instrument and a remote microimager (RMI). LIBS provides elemental emission spectra for 350–550  $\mu\text{m}$  sized observation points on rocks up to a 7 m standoff distance [*Wiens et al.*, 2012; *Maurice et al.*, 2012]. The RMI records high-resolution images of target points before and after LIBS observations, allowing visual identification of and context for each observation point [*Le Mouélic et al.*, 2015]. Mastcam images are also recorded for each ChemCam target using the 100 mm focal length camera (Right Mastcam) [*Malin et al.*, 2010] to provide geologic context and color images.

Boron is observed in LIBS data via neutral atomic emission lines at 249.75 and 249.84 nm (Figure S1a) [*Sansonetti and Martin*, 2005]. Peak areas are obtained by fitting a Voigt lineshape to the LIBS spectra [cf. *Rapin et al.*, 2016]. A preliminary calibration curve is created from standards, yielding the relative abundance of boron (see supporting information). Because the majority of ChemCam targets in Gale contain  $\sim 18$  wt %  $\text{FeO}_T$  [*Mangold et al.*, 2017], interference from a Fe II emission line at 249.96 nm (Figure S2) limits boron detection in Mars data to targets with  $\leq 10$  wt %  $\text{FeO}_T$ . Laboratory LIBS spectra on standards show that B peaks in samples with  $\sim 0.05$  wt % B abundance are visible in samples containing  $\sim 11$  wt %  $\text{FeO}_T$ , and the detection limit is  $\sim 100$  ppm B in Fe-free standards. The detection limit is defined here as the composition at which the boron peak is visible above background noise plus the average area of any interfering lines (Figure S2). Most low Fe observations correspond to  $\text{CaSO}_4$ -filled veins or high silica targets [e.g., *Morris et al.*, 2016; *Frydenvang et al.*, 2017]. In vein targets, the main interfering line is Ca III (249.84 nm) rather than Fe. The statistical significance of boron detections on Mars are calculated from interfering line average peak area and standard deviation are.

## 3. Results

Boron is observed in 43 vein targets (45  $2\sigma$  detections and 30  $3\sigma$  detections totaling 98 observation points) (Figure 1, Table S1, Figure S1). We estimate a detection limit of  $\sim 100$  ppm B in LIBS spectra and boron abundances in veins up to 500 ppm B based on preliminary laboratory studies of boron-bearing standards (see supporting information). Boron was detected in five calcium sulfate vein targets in the Yellowknife Bay Group “Sheepbed” member mudstone, “Point Lake,” and “Shaler” sandstone (Figure 2, inset A) and in 38 veins in the Mt. Sharp Group Murray mudstone and Stimson sandstone (Figure 2). Although veins were targeted on rare occasions during the traverse through the Bradbury Group after visiting Yellowknife Bay, no boron was detected there (Figure 2). The first observation of boron coincided with the first ever vein observation by ChemCam on Martian day (sol) 113 of the mission [*Nachon et al.*, 2014], but the majority of detections



**Figure 1.** Three examples of boron detections in Murray unit vein targets. (a–c) Mastcam context images with RMI footprints (red outlines), (d–f) colorized RMIs labeled with point observations (numbered crosshairs), and (g–i) example LIBS spectra with boron and iron line fits for “Khoabendus” (sol 1380), “Catabola” (sol 1443), and “Cadillac\_Mountain” (sol 1504) (Mastcam images 1381MR0067690000701773E01, 1444MR0071420000702955E01, and 1504MR0076390000404439E01).

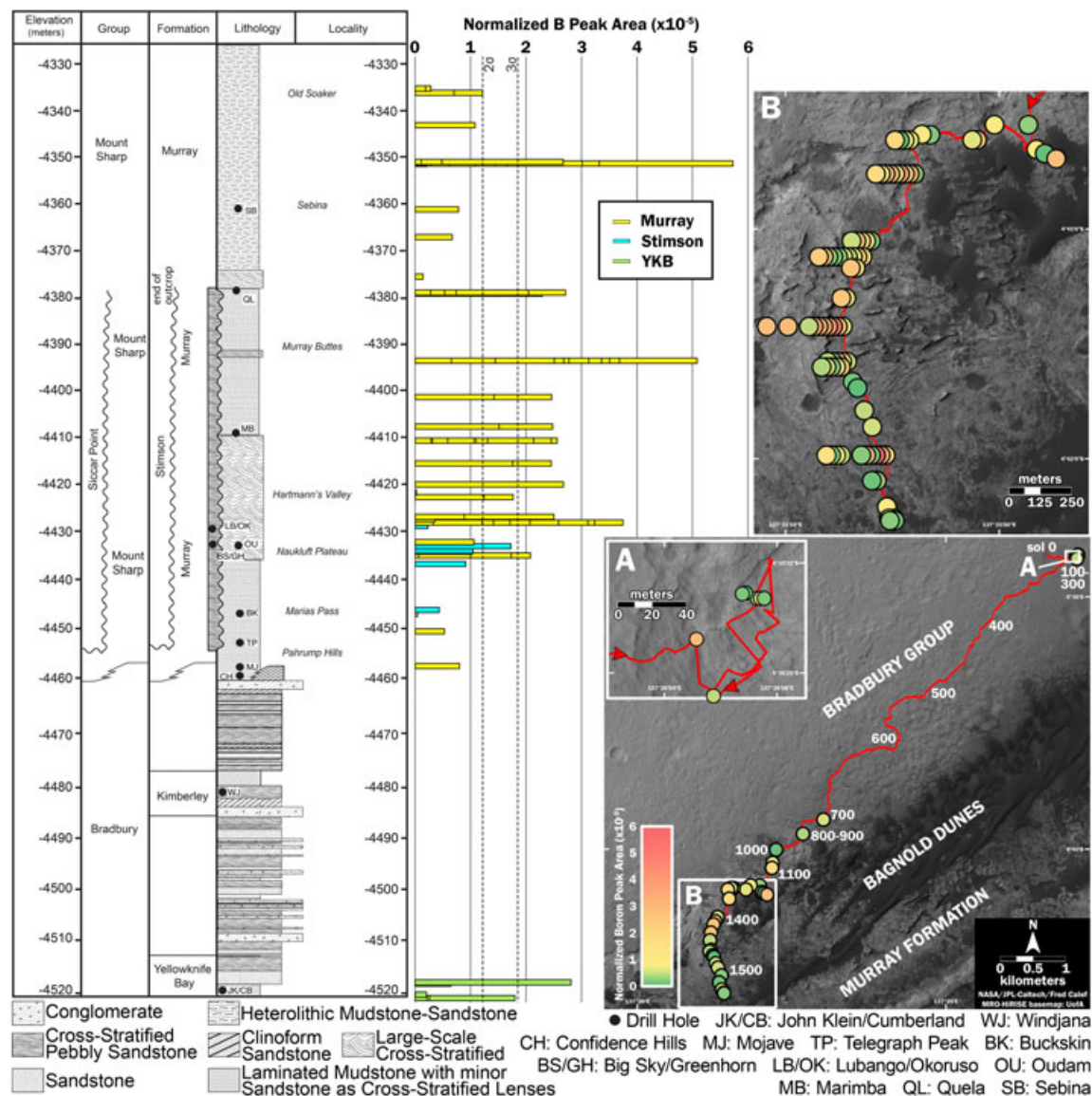
have been made since sol 1350 in Upper Murray veins, at elevations above  $-4435$  m (Figure 2, inset B), and are colocated with clay-rich Murray bedrock [Rampe *et al.*, 2017a].

Boron has been detected in a variety of calcium sulfate vein morphologies and settings (Table S1). Boron does not preferentially appear in any one vein morphology. Vein targets in Yellowknife Bay include the ubiquitous thin ( $<2$  cm) veins, veins with nodular textures, small nodules or “bowls,” polygonal textures, and “protruding” veins (e.g., Figure 1b) [Nachon *et al.*, 2014]. Subsequent investigations of veins in the Murray and Stimson bedrock units [Nachon *et al.*, 2017] found complex and large veins ( $>2$  cm wide) in the “Pahrump Hills” region. The only detection of boron in Pahrump Hills was the “Indianola” target, which is a light-toned part of a large vein in the “Garden City” outcrop. Other targets found after “Naukluft Plateau” include “horizontal veins” that are approximately parallel to mudstone laminations as seen directly above the “Cadillac\_Mountain” target (Figure 1c).

#### 4. Discussion

All boron detections in Gale crater are in veins. However, the lack of detections in bedrock targets is very likely a consequence of observation bias: since Fe and B emission lines interfere with each other in the LIBS spectra, boron detection is limited to targets with  $\leq 10$  wt %  $\text{FeO}_T$ , which represents unusually low Fe for Gale bedrock. Nevertheless, the vein geological context points to emplacement of boron by water. Boron is very easily oxidized; boron is always a borate in conditions where water is stable and in past and present Mars surface oxygen fugacity conditions, which implies that the boron was a borate when emplaced and remains a borate at present [Ingri, 1963; Schubert, 2015]. We suggest that the boron was at least partly emplaced by a late-stage groundwater and was likely redistributed from a primary source [cf. Schwenzer *et al.*, 2016]. Although the iron





**Figure 2.** (left) Gale Crater stratigraphic column [Fedó et al., 2017] with normalized boron peak area for each boron detection plotted as bars versus elevation. Dashed lines correspond to the  $2\sigma$  and  $3\sigma$  significance of each detection. Bar colors represent target geologic unit. (right) The rover traverse map showing the locations of each boron detection. Dot colors represent the normalized boron peak area according to the color bar. Inset A: an expanded map of Yellowknife Bay (sols 100–300). Inset B: an expanded map of targets since sol 1169.

content of typical bedrock targets on Mars precludes reliable measurement of boron, boron may indeed be present in these materials.

#### 4.1. Models for Boron Enrichment in Veins

There are several possible mechanisms of boron enrichments in veins, and each has intriguing implications for Mars. Both models considered suggest that boron (a) weathered out of primary igneous crust in the Gale crater watershed [Ehlmann and Buz, 2015], (b) was dissolved in lake water, and (c) was dissolved in the late-stage groundwater system. However, the different possible mechanisms of initial boron concentration from lake waters have important consequences for fluid pH and the resultant borate mineralogy, since possible borate mineral precipitates are dependent on fluid temperature, pH, and composition [Hunt et al., 1966; Garrett, 1998; Schubert, 2015].

The temperature of the vein-emplacing fluids may be constrained using a number of observations. First, calcium sulfate veins in Gale are predominantly composed of bassanite ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) [Rapin et al., 2016],

which likely forms from the dehydration of gypsum due to hyperarid conditions. This interpretation is consistent with mineralogical results from CheMin [Vaniman *et al.*, 2017]. The presence of gypsum indicates that the groundwater was  $<60^{\circ}\text{C}$  [Rapin *et al.*, 2016]. Other studies of sulfate veins and phyllosilicates in the crater suggest an upper limit of  $\sim 50^{\circ}\text{C}$  [Vaniman *et al.*, 2014; Schwenzer *et al.*, 2016; Nachon *et al.*, 2014, 2017]. Thus, the majority of groundwaters in Gale were likely low temperature.

Fluid pH is the main driver of borate-rock interaction, but pH of Gale groundwater is not well constrained. While most evidence suggests that Gale was host to neutral to alkaline groundwater [e.g., Frydenvang *et al.*, 2017; Hurowitz *et al.*, 2017], some observations suggest that acidic groundwater (pH  $<6$ ) may have interacted with the bedrock [Yen *et al.*, 2017; Hausrath *et al.*, 2017; Rampe *et al.*, 2017b]. Borate species form alkaline solutions with water, providing more evidence that Martian groundwater was alkaline. Although we have no constraints on the concentration of the other ions in solution that affect groundwater pH, when in solution with pure water, borate acts as a buffer with pH  $\sim 9$ . Thus,  $\sim 100$  ppm of boron in solution will tend to make the fluid alkaline, preventing pH shifts outside of pH 8–10. Higher dissolved borate concentrations increase the effectiveness of the buffer. At elevated pH, borates can be adsorbed to 2:1 phyllosilicates and the concentration of borates in clays has been used as a proxy for terrestrial paleosalinity [Fredrickson and Reynolds, 1960; Lerman, 1966; Harder, 1970; Perry, 1972]. The borate anion is adsorbed by positively charged sites on the surfaces of 2:1 phyllosilicates that form in alkaline fluids. The optimal pH for uptake of borates by clays depends on the type of clay and fluid pH, with a pH range for terrestrial clays of  $\sim 8.5$ –10 [Couch and Grim, 1968; Keren and Mezuman, 1981; Keren and O'Conner, 1982; Karahan *et al.*, 2006] at low temperatures  $<120^{\circ}\text{C}$  [You *et al.*, 1996]. Additionally, borates can adsorb to amorphous materials in soils in similar pH conditions to clays, depending on the oxide [Goldberg, 1997]. While the degree of borate adsorption to Fe- and Mg-rich 2:1 phyllosilicates and its relationship with pH is not well constrained for Martian conditions, studies of common terrestrial soil uptake of B [Goldberg, 1997] can be used to estimate that  $\sim 100$ –1000 ppm of B could be adsorbed by clays and amorphous materials in favorable conditions.

With these constraints in mind, we consider two models to explain the observed boron in veins. The first model involves initial adsorption of boron by phyllosilicates and amorphous materials during their deposition in the lake, followed by later groundwater interaction with bedrock to extract the boron before it was coprecipitated with Ca-sulfates in veins. The second model involves initial enrichment of boron in evaporite layers of sulfate, borate, and chloride salts stratigraphically higher in Mt. Sharp, followed by later groundwater dissolution of the evaporites, transport to underlying layers, and coprecipitation of the salts in fractures.

In the first model, borates dissolved in Gale lake water adsorbed on to phyllosilicates and amorphous materials as the lacustrine bedrock was deposited. Later, borate ions may have been mobilized by groundwater and re-emplaced in veins. This model is supported by the observation that the lacustrine Murray and Yellowknife Bay units that host the highest abundance of boron-bearing veins are rich in 2:1 phyllosilicates and amorphous phases [Rampe *et al.*, 2017a; Bristow *et al.*, 2017]. Hence, postlithification interactions of groundwater with these clay-amorphous-rich deposits could lead to boron being desorbed from the bedrock and then precipitated in veins. Groundwater with a low pH or with constituents that have a stronger affinity than borates to clay or amorphous materials could release borates back into solution and lead to borate enrichments in fracture filling materials. Yellowknife Bay pore fluids may have reached pH  $\sim 12$  [Bridges *et al.*, 2015], which could release any boron from or inhibit boron adsorption to clay and amorphous materials. If the borate is adsorbed by the bedrock in water with pH of 9, then fluids of pH 6–7 would be sufficient to free the majority of the borate anions trapped in the bedrock.

Although boron adsorption on to clays and amorphous materials is plausible, many observations suggest that this first model is unlikely because of the likely fluid pH ranges that were present in Gale Lake. Lake waters were near neutral to alkaline pH [Vaniman *et al.*, 2014; Hurowitz *et al.*, 2017]; optimal adsorption of boron to clays and amorphous materials occur at higher alkalinities (pH 8.5–10), and boron adsorption to these materials at pH 6–7 is not favored. Borate concentration in the lake was likely low during deposition of clay- and amorphous-bearing mudstone because it is only present in extremely low concentrations in the crust (Table 1). Thus, boron concentration requires both extensive weathering in the Gale watershed region and subsequent concentration by evaporation of water, e.g., in a closed drainage basin. In a deep near-neutral pH lake [Hurowitz *et al.*, 2017], conditions would not have been conducive to adsorption of borate to clay or amorphous materials.

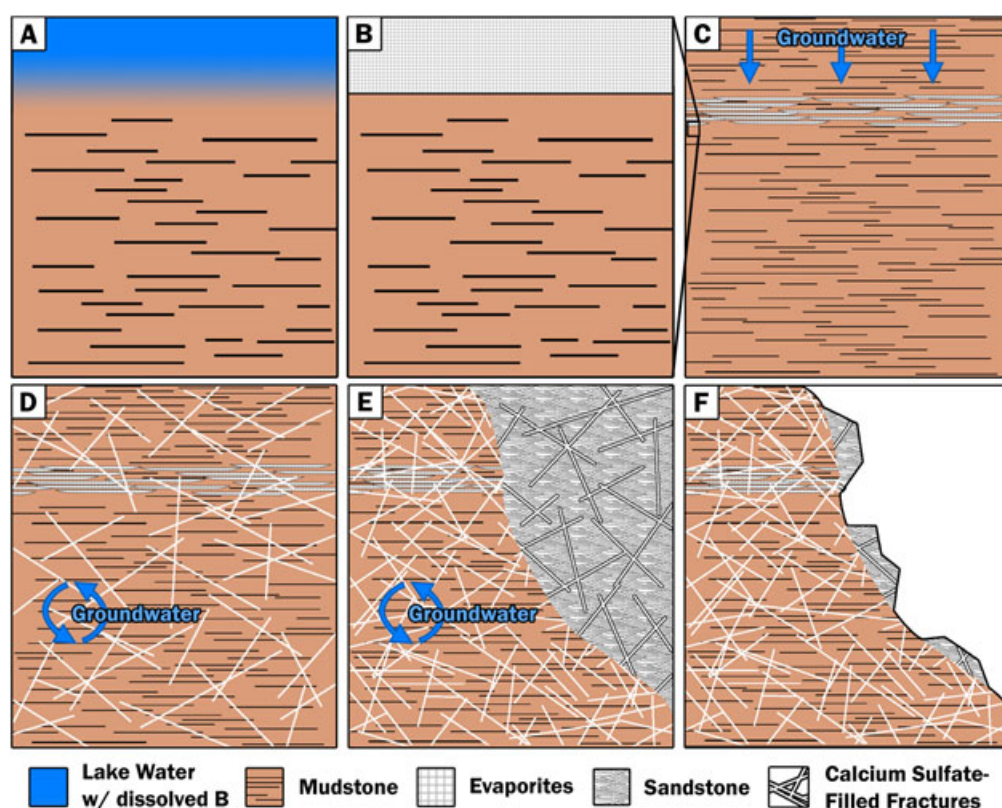
In the second model, borates previously deposited in evaporite layer deposits were remobilized by a subsequent wet period or circulation of basinal fluids after burial. This boron-bearing groundwater could then have precipitated borates in evaporite veins in lower strata. This scenario is supported by the fact that borates are highly soluble in water and in very arid environments on Earth are typically found in evaporites.

Although a primary source of boron-bearing evaporates has yet to be discovered, remote sensing studies suggest that sulfate/phylosilicate layers above the rover's current location in the Murray formation could represent the source evaporitic layer [Milliken *et al.*, 2010; Baldridge *et al.*, 2009; Grotzinger *et al.*, 2015; Fraeman *et al.*, 2016]. During the transition to a drier Mars climate, the Gale crater basin could have been analogous to saline playa lakes in Western Australia, where acidic and alkaline groundwater interact, leading to the coetaneous deposition of clays and sulfates [Baldridge *et al.*, 2009]. Alternatively, Gale could have hosted a perennial lake system such as those in Death Valley California, where layers of borates and other evaporites build up between mudstone deposits after multiple wet-dry cycles [Eugster and Hardie, 1978; Lowenstein *et al.*, 1999; Tanner, 2002]. Later groundwater interaction with these evaporite layers could dissolve some or all of the salts, transporting them into underlying layers of mudstone through fractures [Schwenzer *et al.*, 2016]. This hypothesis is supported by the observation of possible desiccation features in the Upper Murray [Stein *et al.*, 2017]. More broadly, evaporite deposits have been remotely detected on Mars throughout the Southern Highlands [Osterloo *et al.*, 2008; Hynes *et al.*, 2015; Ehlmann and Buz, 2015] and evaporite phases including halite are common in nakhlite martian meteorites [Gooding *et al.*, 1991; Bridges and Grady, 2000; Hicks *et al.*, 2014]. Boron has recently been observed in the Martian meteorite Nakhla in association with halite and carbonaceous material [Thomas-Keptra *et al.*, 2015]. ChemCam has observed chlorine and high sodium that may be interpreted as possible halite or sodium perchlorate in the same vicinity as boron-bearing vein targets [Thomas *et al.*, 2017]. This model may be tested by searching for evaporate deposits as the rover continues its traverse up the Mt. Sharp stratigraphy.

Based on the chemical and stratigraphic evidence presented above, we find the second scenario the more plausible of the two models for B emplacement into veins (Figure 3). The initial deposition of B in evaporites required drying the lake, lowering the water table, remobilizing soluble elements (primarily Ca, Mg, and Na), and precipitating them in evaporite veins lower in the stratigraphy (Figure 3). Deep lake water conditions prevented borate adsorption onto phyllosilicates or amorphous materials (Figure 3a), thus leading to formation of boron-bearing evaporites as Gale lake dried (Figure 3b). Gale then became a predominately closed-drainage basin, forming a perennial lake system; following terrestrial models, layers of mudstone and evaporites would alternate in the bedrock (Figure 3c) [Eugster and Hardie, 1978]. In this perennial lake stage, the shallow lake would have higher borate concentrations and borates could then be adsorbed by lakebed clay and amorphous materials. Later, Gale underwent multiple episodes of eolian burial and exhumation [Grotzinger *et al.*, 2015; Banham *et al.*, 2017; Frydenvang *et al.*, 2017] and burial overpressure plus groundwater intrusion caused fractures to form within the bedrock [Watkins *et al.*, 2017]. Groundwater events then dissolved some of the evaporite deposits (Figure 3d), and the observed evaporite minerals (Ca sulfates) were then coprecipitated with borates in veins throughout the lower stratigraphic layers. The groundwater was enriched in borate from dissolution of the evaporites, implying that the water was alkaline, and borate would be adsorbed to host-rock clay and amorphous components as the boron-rich groundwater circulated through lower stratigraphic layers. The Murray unit then experienced erosion and exhumation before the deposition of the overlying aeolian Stimson sandstone, which itself became lithified and fractured [Grotzinger *et al.*, 2015; Frydenvang *et al.*, 2017; Banham *et al.*, 2017; Watkins *et al.*, 2017]. Fractures in Stimson then also became filled with calcium sulfate and borate (Figure 3e). The groundwater system likely shut down sometime after the deposition of sulfate into the fractures (Figure 3e) but before the erosion of Gale sediments to its present surface (Figure 3f).

ChemCam cannot directly measure mineralogy, but the possible mineralogies of borate-bearing materials in veins may be inferred for a Ca-rich, 0–60°C, and alkaline fluid (for other conditions, see supporting information). The borate anion may isomorphically replace sulfate in the Ca-sulfate minerals in the veins during burial [e.g., Orti and Alonso, 2000], or borates are present as their own phase that coprecipitated with Ca sulfates as Ca borates and Ca sulfate stability field conditions significantly overlap [Crowley, 1996].





**Figure 3.** An illustration of the hypothesized steps that lead from boron dissolved in Gale lake to the present day observation of boron in veins. Starting with a) boron dissolved in lake water, followed by b) evaporite deposition, c) groundwater infiltration, d–e) evaporite remobilization by groundwater, and redistribution of dissolved salts into fractures within the Murray mudstone and Stimson sandstone units, and ending with f) erosion to the present surface. White diagonal lines in d–f represent Ca-sulfate in fractures. Based on events described by Grotzinger *et al.* [2015] and Frydenvang *et al.* [2017].

#### 4.2. Implications for Astrobiology

The presence of boron on Mars opens up new possibilities for habitability because of the important role borate may have played in prebiotic chemistry on early Earth [Scorei, 2012]. Borates stabilize ribose, the simple sugar that forms the backbone of RNA with phosphate [Ricardo *et al.*, 2004; Furukawa *et al.*, 2013]. Without borates, ribose quickly decomposes in water [Larralde *et al.*, 1995]. Borates may thus have been a necessary bridge from abiotically produced organic molecules to RNA-based protolife on Earth [Scorei, 2012]. Although other methods are proposed for producing RNA [Ruiz-Mirazo *et al.*, 2014], this work nevertheless shows that borate is available in an ancient planetary setting. On Mars, we have shown borate was present in a long-lived hydrologic system, suggesting that important prebiotic chemical reactions could plausibly have occurred in the groundwater, if organics were also available. Thus, the discovery of boron in Gale crater opens up intriguing questions about whether life could have arisen on Mars.

The timing of the initial concentration of borates in sediments provides key bounds for when life could have formed on Mars. It is unknown if borate evaporite minerals were present on the Archean Earth [Grew *et al.*, 2011], but the borate evaporites in Gale are much older than the oldest inferred age of evaporites on Earth [Grew *et al.*, 2011]. Additionally, there is evidence for ancient, evolved igneous rocks from the Southern Highlands in the Gale lake watershed [e.g., Cousin *et al.*, 2017], which are required precursor rocks for boron enrichment [Grew *et al.*, 2011]. Hence, the presence of boron enrichments in Gale suggests that boron-concentrating processes can occur early in a terrestrial planet's history. If the primary deposition of borate was in evaporite layers, such as those that form in perennial lakes, borates would be both highly concentrated and in close proximity to clays and any organics, if present. Such wet and dry cycles occurring in perennial lakes are considered ideal for promoting prebiotic reactions on Earth [Lahav and Chang, 1976, 1982]. Additionally, evidence for boron in veins in the younger



Stimson sandstone suggests that the groundwater system in Gale crater was late-stage [Frydenvang *et al.*, 2017]. And although the source of groundwater in Gale crater is as of yet unknown, it is clear that Gale has undergone multiple episodes of groundwater over its history with changes to its chemistry, pH, and Eh over time [Schwenzer *et al.*, 2016; L'Haridon *et al.*, 2017; Lanza *et al.*, 2016; Frydenvang *et al.*, 2017; Yen *et al.*, 2017; Nachon *et al.*, 2017]. This complex and changing groundwater system was not only habitable, providing geochemical and energy gradients needed to support life, but it would also have promoted pre-biotic chemical reactions between borates and any organics present. If borate-organic molecules are directly observed in Gale, the early hydrologic system on Mars may shed light on how life arose on Earth while also opening up new possibilities for life on Mars. The discovery of boron on Mars makes the search for borates a high priority for *Curiosity* and future missions to Mars.

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### References

- Anderson, D. E., *et al.* (2017), Characterization of Laser-Induced Breakdown Spectroscopy (LIBS) emission lines for the identification of chlorides, carbonates, and sulfates in salt/basalt mixtures for the application to MSL ChemCam data: LIBS Cl, C, & S in salt-basalt mixtures, *J. Geophys. Res. Planets*, 122, 744–770, doi:10.1002/2016JE005164.
- Baldridge, A. M., S. J. Hook, J. K. Crowley, G. M. Marion, J. S. Kargel, J. L. Michalski, B. J. Thomson, C. R. de Souza Filho, N. T. Bridges, and A. J. Brown (2009), Contemporaneous deposition of phyllosilicates and sulfates: Using Australian acidic saline lake deposits to describe geochemical variability on Mars, *Geophys. Res. Lett.*, 36, L19201, doi:10.1029/2009GL040069.
- Banham, S. M., *et al.* (2017), The Stimson formation: Determining the morphology of a dry aeolian dune system and its climatic significance in Gale Crater, Mars, paper presented at 48th lunar and planetary science conference, The Woodlands, Tex., Abstract 2014.
- Blake, D., *et al.* (2012), Characterization and calibration of the CheMin mineralogical instrument on Mars science laboratory, *Space Sci. Rev.*, 170(1–4), 341–399, doi:10.1007/s11214-012-9905-1.
- Boutlerow, M. A. (1861), Formation synthétique d'une substance sucrée, *C. R. Hebd. Seances Acad. Sci.*, 53, 147–147.
- Bridges, J. C., and M. Grady (2000), Evaporite mineral assemblages in the nakhlite (Martian) meteorites, *Earth Planet. Sci. Lett.*, 176(3–4), 267–279, doi:10.1016/S0012-821X(00)00019-4.
- Bridges, J. C., S. P. Schwenzer, R. Leveille, F. Westall, R. C. Wiens, N. Mangold, T. Bristow, P. Edwards, and G. Berger (2015), Diagenesis and clay mineral formation at Gale Crater, Mars, *J. Geophys. Res. Planets*, 120, 1–19, doi:10.1002/2014JE004757.
- Bristow, T. F., *et al.* (2017), Surveying clay mineral diversity in the Murray formation, Gale crater, Mars, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 2462.
- Cloutis, E., B. Berg, P. Mann, and D. Applin (2016), Reflectance spectroscopy of low atomic weight and Na-rich minerals: Borates, hydroxides, nitrates, nitrites, and peroxides, *Icarus*, 264, 20–36, doi:10.1016/j.icarus.2015.08.026.
- Clegg, S. M., E. C. Sklute, M. D. Dyar, J. E. Barefield, and R. C. Wiens (2008), Quantitative analysis of samples with variable composition by remote laser-induced breakdown spectroscopy, paper presented at 7th International Conference on Mars, Pasadena, Calif., Abstract 3216.
- Clegg, S. M., *et al.* (2017), Recalibration of the Mars Science Laboratory ChemCam instrument with an expanded geochemical database, *Spectrochim. Acta, Part B*, 129, 64–85, doi:10.1016/j.sab.2016.12.003.
- Couch, E. L., and R. E. Grim (1968), Boron fixation by illites, *Clay Clay Miner.*, 16(3), 249–256, doi:10.1346/CCMN.1968.0160307.
- Cousin, A., *et al.* (2017), Classification of igneous rocks analyzed by ChemCam at Gale crater, Mars, *Icarus*, 288, 265–283, doi:10.1016/j.icarus.2017.01.014.
- Crowley, J. K. (1996), Mg- and K-bearing borates and associated evaporites at eagle borax spring, Death Valley, California: A spectroscopic exploration, *Econ. Geol.*, 91(3), 622–635.
- Edgett K. S. and M. C. Malin (2001), Rock stratigraphy in Gale crater, Mars, paper presented at 32nd Lunar and Planetary Science Conference, Houston, Tex., Abstract 1005.
- Ehlmann, B. L., and J. Buz (2015), Mineralogy and fluvial history of the watersheds of Gale, Knobel, and Sharp craters: A regional context for the Mars science laboratory *Curiosity's* exploration, *Geophys. Res. Lett.*, 42, 264–273, doi:10.1002/2014GL062553.
- Eugster, H. P., and L. A. Hardie (1978), Saline Lakes, in *Lakes: Chemistry, Geology, Physics*, edited by A. Lerman, pp. 237–293, Springer, New York, New York.
- Fedo, C. *et al.* (2017), Facies analysis and basin architecture of the upper part of the Murray formation, Gale crater, Mars, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 1689.
- Fraeman, A. A., B. L. Ehlmann, R. E. Arvidson, C. S. Edwards, J. P. Grotzinger, R. E. Milliken, D. P. Quinn, and M. S. Rice (2016), The stratigraphy and evolution of lower Mount Sharp from spectral, morphological, and thermophysical orbital data sets, *J. Geophys. Res. Planets*, 121, 1713–1736, doi:10.1002/2016JE005095.
- Fredrickson, A. F., and R. C. Reynolds (1960), Geochemical method for determining paleosalinity, *Clay Clay Miner.*, 8, 203–213.
- Frydenvang, J., *et al.* (2017), Diagenetic silica enrichment and late-stage groundwater activity in Gale crater, Mars, *Geophys. Res. Lett.*, 44, 4716–4724, doi:10.1002/2017GL073323.
- Furukawa, Y., M. Horiuchi, and T. Kakegawa (2013), Selective stabilization of ribose by borate, *Orig. Life Evol. Biosph.*, 43(4–5), 353–361, doi:10.1007/s11084-013-9350-5.
- Garrett, D. E. (1998), *Borates: Handbook of Deposits, Processing, Properties, and Use*, Academic Press, San Diego, Calif.
- Grew, E. S., J. L. Bada, and R. M. Hazen (2011), Borate minerals and origin of the RNA world, *Orig. Life Evol. Biosph.*, 41(4), 307–316, doi:10.1007/s11084-010-9233-y.
- Goldberg, S. (1997), Reactions of boron with soils, *Plant Soil*, 193(1–2), 35–48, doi:10.1023/A:1004203723343.
- Goldschmidt, V. M. and C. Peters (1932), Zur Geochemie des Bor, *Nachr. Gesellch. Naturwissensch. Göttingen, Math. Phys. Klasse* 111, 25, 402.
- Gooding, J. L., S. J. Wentworth, and M. E. Zolensky (1991), Aqueous alteration of the Nakhla meteorite, *Meteorit. Planet. Sci.*, 26(2), 135–144, doi:10.1111/j.1945-5100.1991.tb01029.x.
- Grotzinger, J. P., *et al.* (2014), A habitable fluvio-lacustrine environment at Yellowknife Bay, Gale Crater, Mars, *Science*, 343(6169), 1242777, doi:10.1126/science.1242777.
- Grotzinger, J. P., *et al.* (2015), Deposition, exhumation, and paleoclimate of an ancient lake deposit, Gale crater, Mars, *Science*, 350(6257), aac7575–aac7575, doi:10.1126/science.aac7575.

- Harder, H. (1970), Boron content of sediments as a tool in facies analysis, *Sediment. Geol.*, 4(1–2), 153–175, doi:10.1016/0037-0738(70)90009-6.
- Hausrath, E. M., D. W. Ming, T. Peretyazhko, and E. B. Rampe (2017), Using reactive transport modeling to understand formation of the Stimson sedimentary unit and altered fracture zones at Gale crater, Mars, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 2420.
- Hesse, R., P. Streubel, and R. Szargan (2007), Product or sum: Comparative tests of Voigt, and product or sum of Gaussian and Lorentzian functions in the fitting of synthetic Voigt-based X-ray photoelectron spectra, *Surf. Interface Anal.*, 39(5), 381–391, doi:10.1002/sia.2527.
- Hicks, L. J., J. C. Bridges, and S. J. Gurman (2014), Ferric saponite and serpentine in the nakhlite Martian meteorites, *Geochim. Cosmochim. Acta*, 136, 194–210, doi:10.1016/j.gca.2014.04.010.
- Hunt, C. B., T. W. Robinson, W. A. Bowles, and A. L. Washburn (1966), Hydrologic basin, *Death Valley, California*, Professional Paper, Report.
- Hurowitz, J. A., et al. (2017), Redox stratification of an ancient lake in Gale crater, Mars, *Science*, 356(6341), eaah6849, doi:10.1126/science.aah6849.
- Hynek, B. M., M. K. Osterloo, and K. S. Kierein-Young (2015), Late-stage formation of Martian chloride salts through ponding and evaporation, *Geology*, 43(9), 787–790, doi:10.1130/G36895.1.
- Ingri, N. (1963), Equilibrium studies of polyanions containing Bill, SilV, GelV and VV, *Sven. Kem. Tidskr.*, 75(4), 199–230.
- Karahan, S., M. Yurdakoç, Y. Seki, and K. Yurdakoç (2006), Removal of boron from aqueous solution by clays and modified clays, *J. Colloid Interface Sci.*, 293(1), 36–42, doi:10.1016/j.jcis.2005.06.048.
- Keren, R., and U. Mezuman (1981), Boron adsorption by clay minerals using a phenomenological equation, *Clay Clay Miner.*, 29(3), 198–204, doi:10.1346/CCMN.1981.0290305.
- Keren, R., and G. A. O'Conner (1982), Effect of exchangeable ions and ionic strength on boron adsorption by montmorillonite and Illite, *Clay Clay Miner.*, 30(5), 341–346, doi:10.1346/CCMN.1982.0300504.
- Kim, H.-J., A. Ricardo, H. I. Illangkoon, M. J. Kim, M. A. Carrigan, F. Frye, and S. A. Benner (2011), Synthesis of carbohydrates in mineral-guided prebiotic cycles, *J. Am. Chem. Soc.*, 133(24), 9457–9468, doi:10.1021/ja201769f.
- Lahav, N., and S. Chang (1976), The possible role of solid surface area in condensation reactions during chemical evolution: Reevaluation, *J. Mol. Evol.*, 8(4), 357–380, doi:10.1007/BF01739261.
- Lahav, N., and S. Chang (1982), The possible role of soluble salts in chemical evolution, *J. Mol. Evol.*, 19(1), 36–46, doi:10.1007/BF02100222.
- Lanza, N. L., et al. (2016), Oxidation of manganese in an ancient aquifer, Kimberley formation, Gale crater, *Geophys. Res. Lett.*, 43, 7398–7407, doi:10.1002/2016GL069109.
- Lanza, N. L., S. M. Clegg, A. Cousin, O. Forni, M. F. Kirk, S. N. Lamm, A. M. Ollila, V. Payré, and R. C. Wiens (2017), Identifying potential chemical biosignatures in manganese minerals with laser-induced breakdown spectroscopy, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 2913.
- Larralde, R., M. P. Robertson, and S. L. Miller (1995), Rates of decomposition of ribose and other sugars: Implications for chemical evolution, *Proc. Natl. Acad. Sci.*, 92(18), 8158–8160.
- Le Mouélic, S., et al. (2015), The ChemCam remote micro-imager at Gale Crater: Review of the first year of operations on Mars, *Icarus*, 249, 93–107, doi:10.1016/j.icarus.2014.05.030.
- Lerman, A. (1966), Boron in clays and estimation of paleosalinities, *Sedimentology*, 6, 267–286, doi:10.1111/j.1365-3091.1966.tb01895.x.
- L'Haridon, J., N. Mangold, W. Rapin, O. Forni, P.-Y. Meslin, E. Dehouck, M. Nachon, L. Le Deit, O. Gasnault, S. Maurice, R. Wiens (2017), Identification and implications of iron detection within calcium sulfate mineralized veins by ChemCam at Gale crater, Mars, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 1328.
- Lodders, K. (1998), A survey of SNC meteorite whole-rock compositions, *Meteorit. Planet. Sci. Suppl.*, 33, 183–190.
- Lowenstein, T. K., J. Li, C. Brown, S. M. Roberts, T.-L. Ku, S. Luo, and W. Yang (1999), 200 k.y. paleoclimate record from Death Valley salt core, *Geology*, 27(1), 3, doi:10.1130/0091-7613(1999)027<0003:KYPRFD>2.3.CO;2.
- Malin, M. C. (2000), Sedimentary rocks of early Mars, *Science*, 290(5498), 1927–1937, doi:10.1126/science.290.5498.1927.
- Malin, M. C., et al. (2010), The Mars Science Laboratory (MSL), Mast-Mounted Cameras (Mastcams) Flight Instruments, paper presented at 41st Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 1123.
- Mangold, N., et al. (2017), Classification scheme for sedimentary and igneous rocks in Gale crater, Mars, *Icarus*, 284, 1–17, doi:10.1016/j.icarus.2016.11.005.
- Maurice, S., et al. (2012), The ChemCam instrument suite on the Mars science laboratory (MSL) rover: Science objectives and mast unit description, *Space Sci. Rev.*, 170(1–4), 95–166, doi:10.1007/s11214-012-9912-2.
- Milliken, R. E., J. P. Grotzinger, and B. J. Thomson (2010), Paleoclimate of Mars as captured by the stratigraphic record in Gale Crater: Stratigraphy of Gale crater, *Geophys. Res. Lett.*, 37, L04201, doi:10.1029/2009GL041870.
- Morris, R. V., et al. (2016), Silicic volcanism on Mars evidenced by tridymite in high-SiO<sub>2</sub> sedimentary rock at Gale Crater, *Proc. Natl. Acad. Sci.*, 113(26), 7071–7076, doi:10.1073/pnas.1607098113.
- Nachon, M., et al. (2014), Calcium sulfate veins characterized by ChemCam/Curiosity at Gale crater, Mars, *J. Geophys. Res. Planets*, 119, 1991–2016, doi:10.1002/2013JE004588.
- Nachon, M., et al. (2017), Chemistry of diagenetic features analyzed by ChemCam at Pahrump Hills, Gale crater, Mars, *Icarus*, 281, 121–136, doi:10.1016/j.icarus.2016.08.026.
- Orti, F., and R. N. Alonso (2000), Gypsum-Hydroboracite Association in the Sijes Formation (Miocene, NW Argentina): Implications for the genesis of mg-bearing borates, *J. Sediment. Res.*, 70(3), 664–681, doi:10.1306/2DC4092F-0E47-11D7-8643000102C1865D.
- Osterloo, M. M., V. E. Hamilton, J. L. Bandfield, T. D. Glotch, A. M. Baldridge, P. R. Christensen, L. L. Tornabene, and F. S. Anderson (2008), Chloride-bearing materials in the southern highlands of Mars, *Science*, 319(5870), 1651–1654, doi:10.1126/science.1150690.
- Osterloo, M. M., F. S. Anderson, V. E. Hamilton, and B. M. Hynek (2010), Geologic context of proposed chloride-bearing materials on Mars, *J. Geophys. Res.*, 115, E10012, doi:10.1029/2010JE003613.
- Perry, E. A. (1972), Diagenesis and the validity of the boron paleosalinity technique, *Am. J. Sci.*, 272, 150–160.
- Rampe, E. B., et al. (2017a), Mineral trends in early Hesperian lacustrine mudstone at Gale crater, Mars, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 2821.
- Rampe, E. B., et al. (2017b), Mineralogy of an ancient lacustrine mudstone succession from the Murray formation, Gale crater, Mars, *Earth Planet. Sci. Lett.*, 471, 172–185, doi:10.1016/j.epsl.2017.04.021.
- Rapin, W., et al. (2016), Hydration state of calcium sulfates in Gale crater, Mars: Identification of bassanite veins, *Earth Planet. Sci. Lett.*, 452, 197–205, doi:10.1016/j.epsl.2016.07.045.
- Ricardo, A., et al. (2004), Borate minerals stabilize ribose, *Science*, 303(5655), 196–196, doi:10.1126/science.1092464.
- Ruiz-Mirazo, K., C. Briones, and A. Escosura (2014), Prebiotic systems chemistry: New perspectives for the origins of life, *Chem. Rev.*, 114(1), 285–366, doi:10.1021/cr2004844.

- Sansonetti, J. E., and W. C. Martin (2005), Handbook of basic atomic spectroscopic data, *J. Phys. Chem. Ref. Data*, 34(4), 1559–2259, doi:10.1063/1.1800011.
- Schubert, D. M. (2015), Boron: Inorganic chemistry, in *Encyclopedia of Inorganic and Bioinorganic Chemistry*, edited by R. A. Scott, pp. 1–28, John Wiley, U. K.
- Schwenzer, S. P., et al. (2016), Fluids during diagenesis and sulfate vein formation in sediments at Gale Crater, Mars, *Meteorit. Planet. Sci.*, 51(11), 2175–2202, doi:10.1111/maps.12668.
- Scorei, R. (2012), Is boron a prebiotic element? A mini-review of the essentiality of boron for the appearance of life on Earth, *Orig. Life Evol. Biosph.*, 42(1), 3–17, doi:10.1007/s11084-012-9269-2.
- Spivack, A., M. Palmer, and J. Edmond (1987), The sedimentary cycle of the boron isotopes, *Geochim. Cosmochim. Acta*, 51(7), 1939–1949, doi:10.1016/0016-7037(87)90183-9.
- Spivak-Birndorf, L., M. Wadhwa, and L. B. Williams (2008a), The boron isotopic composition of Nakhla iddingsite, paper presented at 39th Lunar and Planetary Science Conference, League City, Tex., Abstract 1904.
- Spivak-Birndorf, L., M. Wadhwa, and L. B. Williams (2008b), Boron isotopic composition of igneous minerals and secondary alteration products in Nakhla paper presented at Ground Truth from Mars: Science Payoff from a Sample Mission, Albuquerque, NM, Abstract 4050.
- Spivak-Birndorf, L., M. Wadhwa, and L. B. Williams (2008c), Boron isotopes in the nakhlites: Implications for crustal fluids on Mars, Paper Presented at Goldschmidt, Vancouver, Canada.
- Stein, N., J. P. Grotzinger, J. Schieber, N. Mangold, H. Newsom, M. Minitti, D. Sumner, K. S. Edgett, K. Stack, C. Fedo, S. Gupta, B. Hallet, A. Vasavada, and D. Fey (2017), Candidate desiccation cracks in the upper Murray formation, Gale crater, Mars, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 2387.
- Stephenson, J. D., L. J. Hallis, K. Nagashima, and S. J. Freeland (2013), Boron Enrichment in Martian Clay, edited by S. Maas, *PLoS ONE*, 8(6), e64624, doi:10.1371/journal.pone.0064624.
- Tanner, L. H. (2002), Borate formation in a perennial lacustrine setting: Miocene–Pliocene furnace creek formation, Death Valley, California, USA, *Sediment. Geol.*, 148(1–2), 259–273, doi:10.1016/S0037-0738(01)00221-4.
- Thomas, N. H., B. L. Ehlmann, D. E. Anderson, W. Rapin, S. Schröder, O. Forni, S. M. Clegg, R. C. Wiens, O. Gasnault and S. Maurice (2017), ChemCam survey of volatile elements in the Murray formation, Gale crater, Mars, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 2756.
- Thomas-Keptra K. L., S. J. Clemett, D. S. McKay, E. K. Gibson and S. J. Wentworth (2015), Indigenous carbonaceous matter and boron associated with halite crystals in Nakhla, paper presented at 46th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 2770.
- Vaniman, D., M. D. Dyar, R. Wiens, A. Ollila, N. Lanza, J. Lasue, J. M. Rhodes, S. Clegg, and H. Newsom (2012), Ceramic ChemCam calibration targets on Mars science laboratory, *Space Sci. Rev.*, 170(1–4), 229–255, doi:10.1007/s11214-012-9886-0.
- Vaniman, D. T., et al. (2014), Mineralogy of a mudstone at Yellowknife Bay, gale crater, Mars, *Science*, 343(6169), 1243480, doi:10.1126/science.1243480.
- Vaniman, D. T., et al. (2017), Calcium sulfates at Gale crater and limitations on gypsum stability, paper presented at 48th lunar and planetary Science Conference, The Woodlands, Tex., Abstract 1661.
- Watkins, J. A., J. P. Grotzinger, and J-P. Avouac (2017) Fracture formation by compaction-related burial in Gale crater, Mars: implications for the origin of Aeolis Mons, paper presented at 48th Lunar and Planetary Science Conference, The Woodlands, Tex., Abstract 3019.
- Wiens, R. C., et al. (2012), The ChemCam instrument suite on the Mars science laboratory (MSL) rover: Body unit and combined system tests, *Space Sci. Rev.*, 170(1–4), 167–227, doi:10.1007/s11214-012-9902-4.
- Wiens, R. C., et al. (2013), Pre-flight calibration and initial data processing for the ChemCam laser-induced breakdown spectroscopy instrument on the Mars Science Laboratory rover, *Spectrochim. Acta, Part B*, 82, 1–27, doi:10.1016/j.sab.2013.02.003.
- Williams, L. B., R. L. Hervig, J. R. Holloway, and I. Hutcheon (2001), Boron isotope geochemistry during diagenesis. Part I. Experimental determination of fractionation during illitization of smectite, *Geochim. Cosmochim. Acta*, 65(11), 1769–1782, doi:10.1016/S0016-7037(01)00557-9.
- Yen, A. S., et al. (2017), Multiple stages of aqueous alteration along fractures in mudstone and sandstone strata in Gale Crater, Mars, *Earth Planet. Sci. Lett.*, 471, 186–198, doi:10.1016/j.epsl.2017.04.033.
- You, C.-F., A. J. Spivack, J. M. Gieskes, J. B. Martin, and M. L. Davisson (1996), Boron contents and isotopic compositions in pore waters: A new approach to determine temperature induced artifacts—Geochemical implications, *Mar. Geol.*, 129(3–4), 351–361, doi:10.1016/0025-3227(96)83353-6.